ARL-TN-0693 ● SEP 2015

US Army Research Laboratory

Theoretical Prediction of the Heats of Formation, Densities and Relative Sensitivities, and/or Synthetic Approaches Toward the Synthesis of High Energy Dense Materials (HEDMs): 3,5-Dinitro-1,3,5-Oxadiazinane, Bis-Adjacent RDX, Bis-Adjacent HMX, 4,4',6,6'-Tetranitro-1,1'-Bis(N-oxide)-5,5',6,6'-4H,4'H-5,5'-Bisimidazo Oxadiazole, and the Open-Cage Derivative of CL-20

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NOTICES

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Weapons and Materials Research Directorate, ARL

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14. ABSTRACT

Using the US Army Research Laboratory (ARL)-developed series of scripts, written to dramatically simplify the computation of crystalline density and heat of formation, we evaluated the performance properties for 5 notional energetic materials: 3,5-dinitro-1,3,5-oxadiazinane, *bis*-adjacent RDX, *bis*-adjacent HMX, 4,4',6,6'-tetranitro-1,1'-bis(*N*-oxide)-5,5',6,6'-4H,4'H-5,5'-bisimidazo oxadiazole, and the open-cage derivative of CL-20. Additionally, a qualitative estimation of the impact sensitivities has been calculated. This technical note outlines the procedures used to generate this information, as well as Cheetah calculations using the predicted crystalline densities and heats of formation. Synthetic efforts toward synthesizing 3,5-dinitro-1,3,5-oxadiazinane, *bis*-adjacent RDX**,** and 4,4',6,6'-tetranitro-1,1'-bis(*N*-oxide)-5,5',6,6'-4H,4'H-5,5'-bisimidazo oxadiazole are described, as well as potential synthetic pathways toward synthesizing, *bis*-adjacent HMX and the open-cage derivative of CL-20.

15. SUBJECT TERMS

computational toolbox, script, crystalline density, heat of formation, impact sensitivity, synthesis, energetic materials

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1. Introduction

US Army Research Laboratory (ARL) researchers have achieved robust theoretical models capable of predicting performance properties, such as heats of formation,[1,2] densities,[3,4] and impact sensitivity[5] of energetic materials (EMs) and have begun growing advanced synthesis capabilities to realize notional materials. This dual capability allows synthetic and formulation chemists to safely and quickly screen candidate materials to focus efforts only on the most promising compounds. For an in depth explanation of the different theoretical methods employed herein, please refer to previous works.[6,7] This technical note will detail theoretical predictions and potential synthesis routes, including efforts to date, for 5 notional EMs: 3,5-dinitro-1,3,5-oxadiazinane (**1**), bis-adjacent RDX (**2**), bis-adjacent HMX (**3**),4,4',6,6'-tetranitro-1,1'-bis(N-oxide)-5,5',6,6'-4H,4'H-5,5'-bisimidazo oxadiazole (**4**), and the open-cage derivative of CL-20 (**5**).

2. Results and Discussion

The properties of the notional 3,5-dinitro-1,3,5-oxadiazinane (**1**, a), bis-adjacent RDX (**2**, b), bis-adjacent HMX (**3**, c), 4,4',6,6'-tetranitro-1,1'-bis(N-oxide)-5,5',6,6'-4H,4'H-5,5'-bisimidazo oxadiazole (**4**, d), and the open-cage derivative of CL-20 (**5**, e) molecules (Fig. 1a–e) were predicted using the ARL tools.[7] For the estimation of the impact sensitivities, the electrostatic maps on the 0.001 isosurfaces were generated with the scalar range of the electrostatic surface potential (ESP) ranging from –0.05 to 0.075. Recall that for this visualization methodology, regions of large positive charge (i.e., electron deficient regions, labeled as red) over the backbone of the structure tend to indicate increased sensitivity.

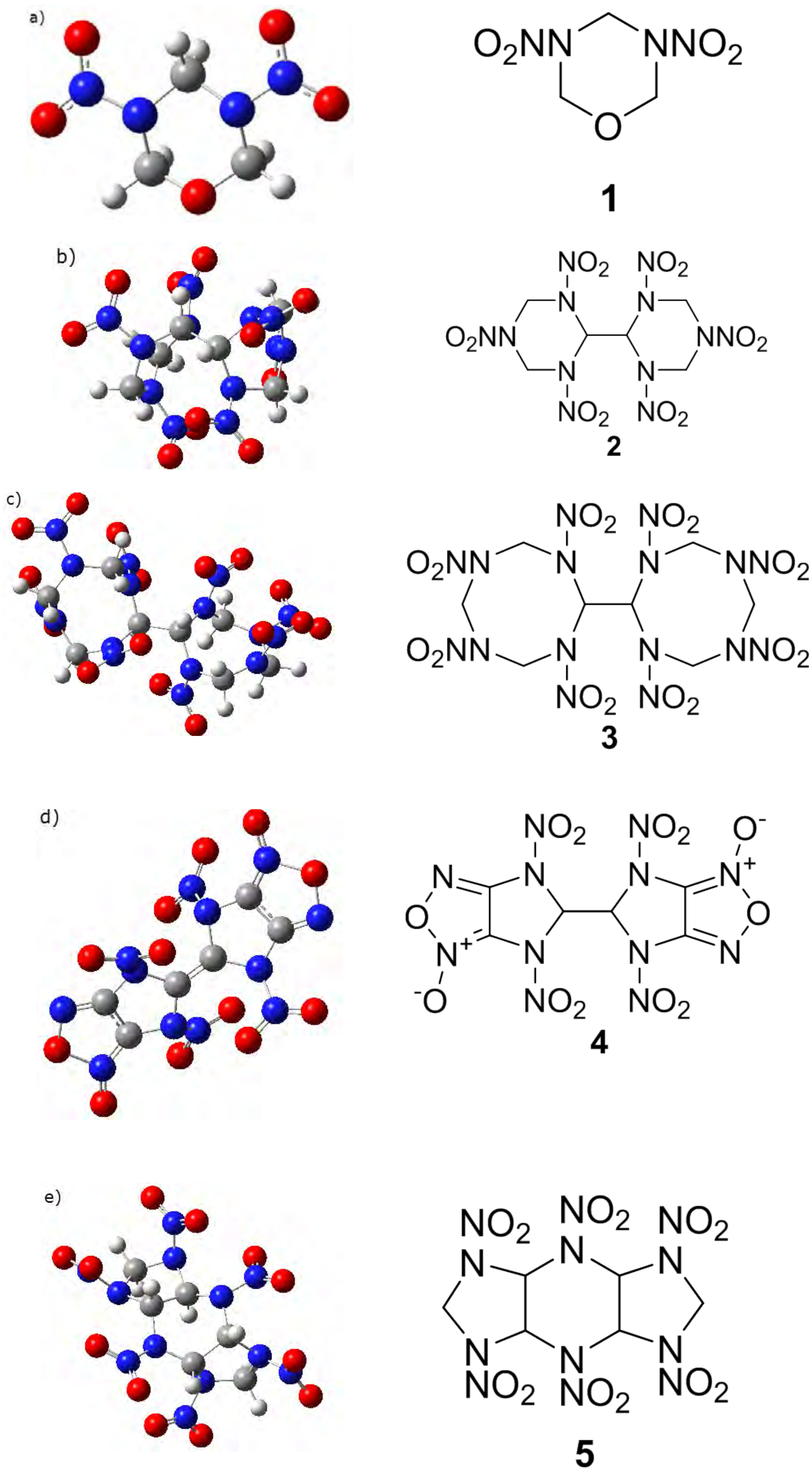


Fig. 1 Optimized structures a) 1, b) 2, c) 3, d) 4, and e) 5

The computed heats of formation and crystalline densities for these molecules are presented in Table 1. Additionally, we plot the ESP maps for **1** (Fig. 2a–b), **2** (Fig. 3a–b), **3** (Fig. 4a–b), **4** (Fig. 5a–b), and **5** (Fig. 6a–b) both with and without the molecule overlaid on the ESP. Analyzing the images, we would quantify the molecules as insensitive for molecule **1**, moderately sensitive for molecules **2** and **4**, and sensitive for molecules **3** and **5**. Recall however, that this methodology is qualitative, and exact values are not determinable. Using the predicted data, we then performed Cheetah 7.0 calculations[8] to predict the performance parameters. At the Chapman-Jouguet (CJ) point, Cheetah yields the values shown in Table 2.

Table 1 Computed heats of formation and crystalline densities for 3,5-dinitro-1,3,5-oxadiazinane (1), bis-adjacent RDX (2), bis-adjacent HMX (3), 4,4',6,6'-tetranitro-1,1'-bis(N-oxide)-5,5',6,6'-4H,4'H-5,5'-bisimidazo oxadiazole (4), and the open-cage derivative of CL-20 (5)

Molecule	Solid Phase Heat of Formation (kcal/mol)	Density (cm^3)
1	–22.213	1.699
2	81.543	1.886
3	82.797	1.919
4	251.902	2.025
5	113.480	1.919

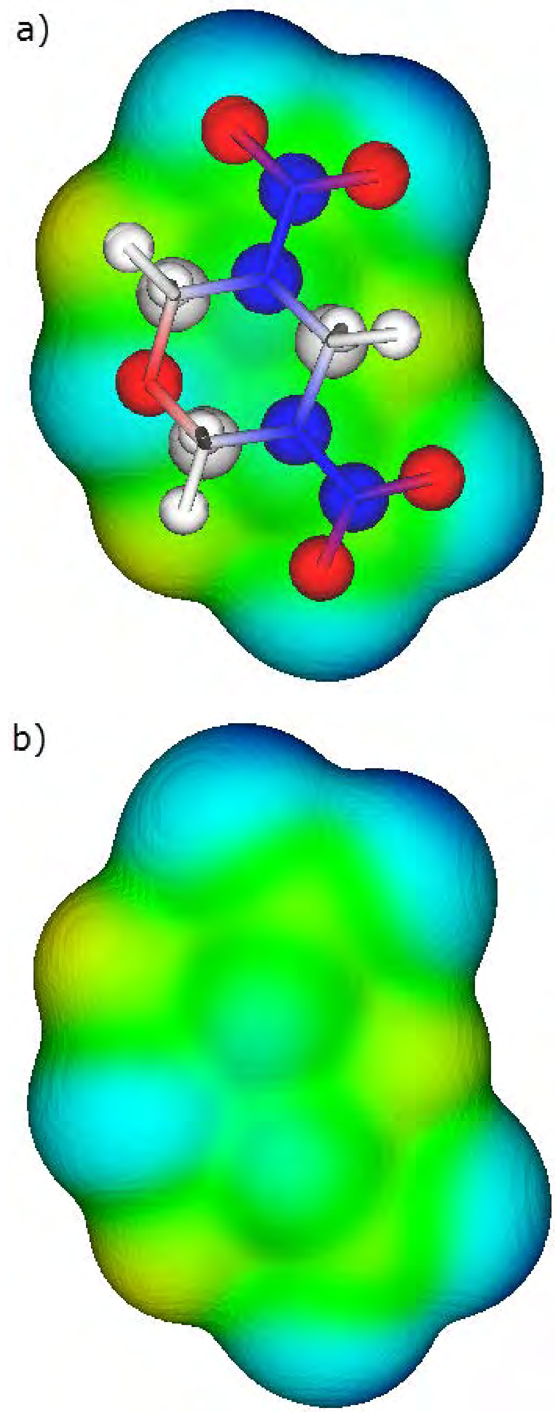


Fig. 2 Electrostatic potential map of 1, a) with and b) without molecule overlay

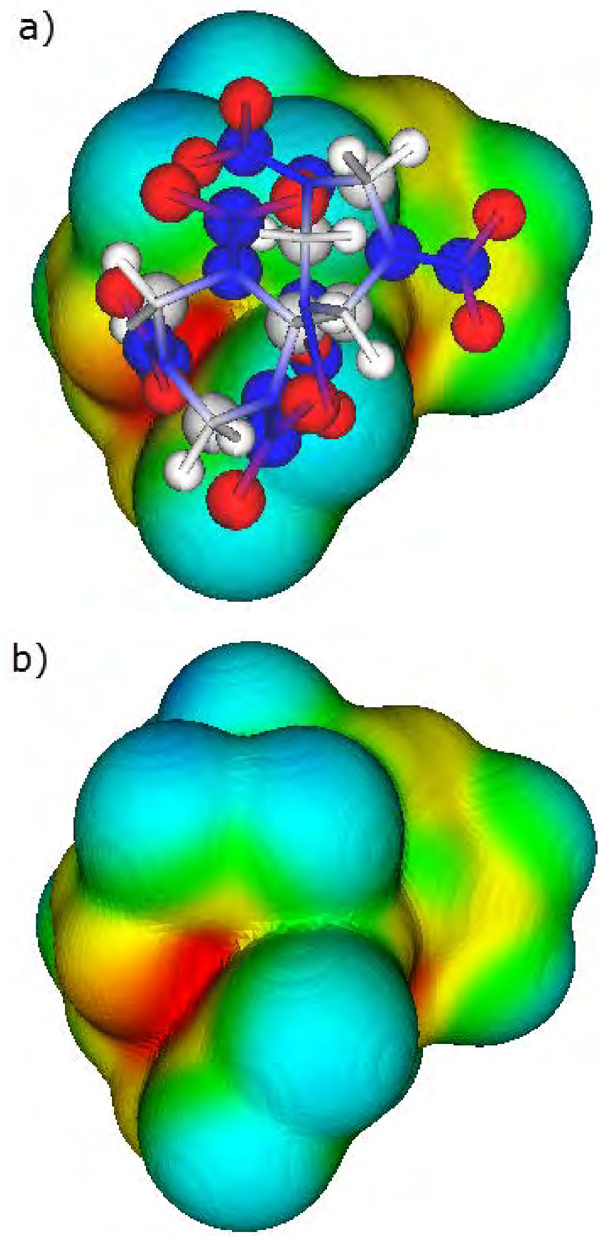


Fig. 3 Electrostatic potential map of 2, a) with and b) without molecule overlay

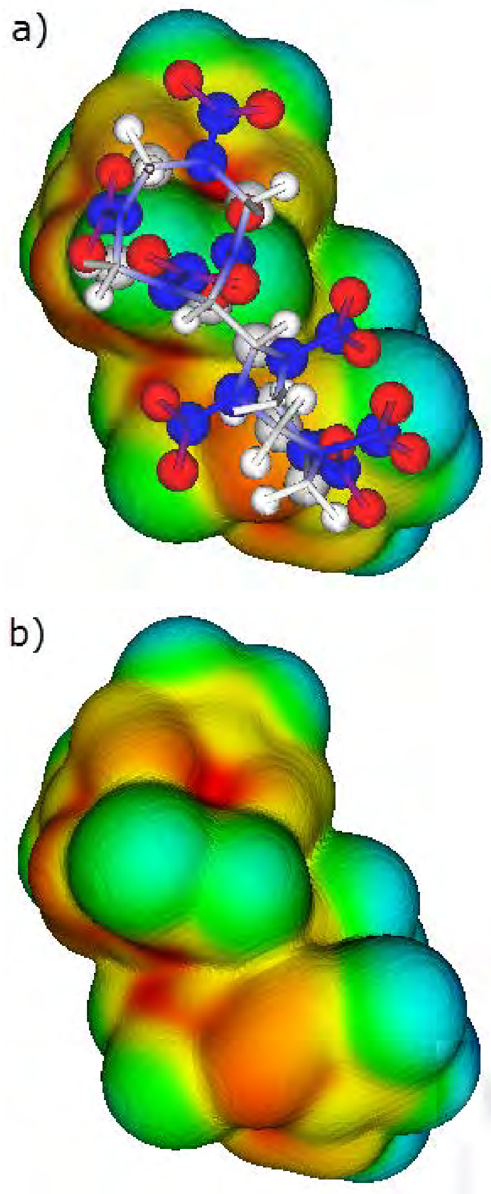


Fig. 4 Electrostatic potential map of 3, a) with and b) without molecule overlay

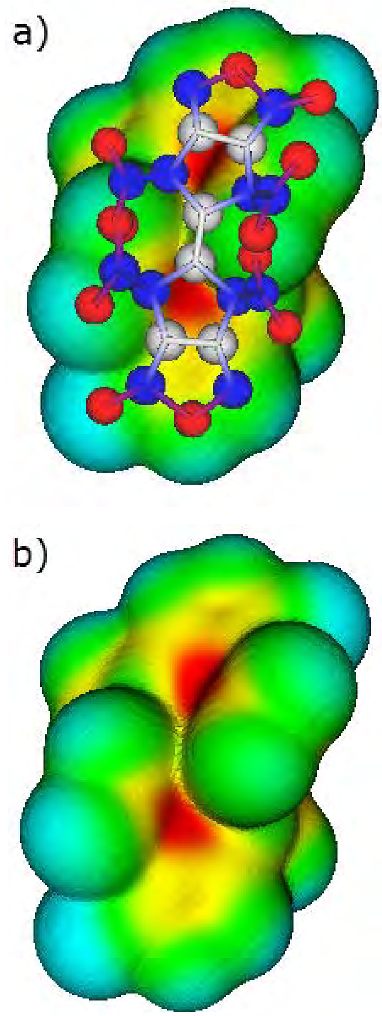


Fig. 5 Electrostatic potential map of 4, a) with and b) without molecule overlay

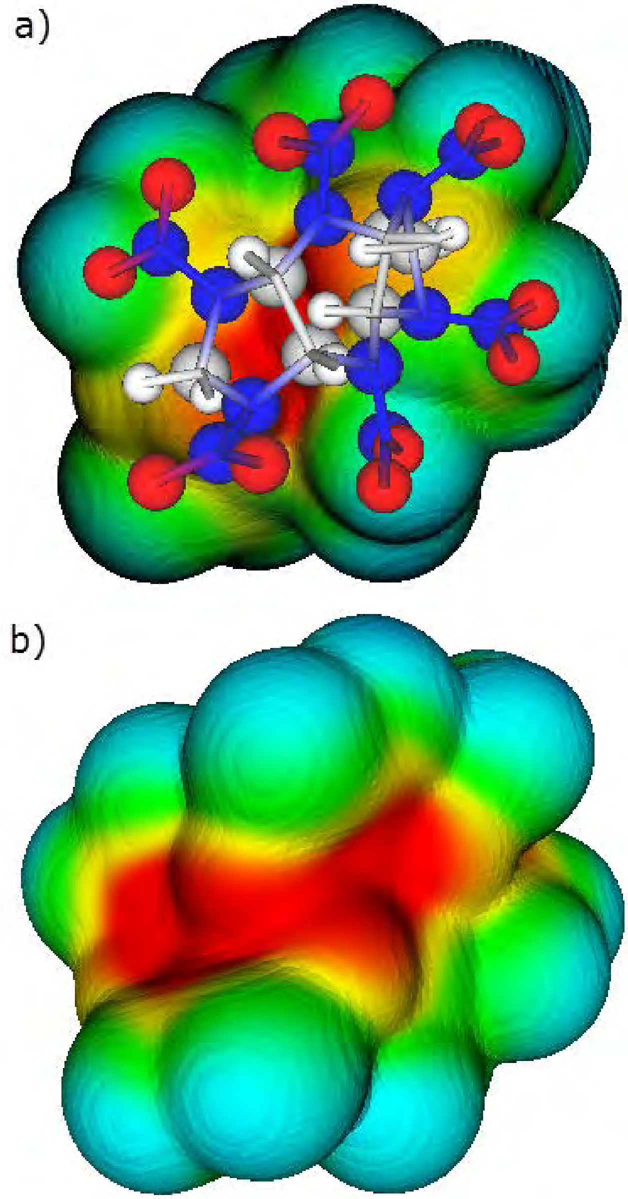


Fig. 6 Electrostatic potential map of 5, a) with and b) without molecule overlay

Table 2 Cheetah predicted properties for 3,5-dinitro-1,3,5-oxadiazinane (1), bis-adjacent RDX (2), bis-adjacent HMX (3), 4,4',6,6'-tetranitro-1,1'-bis(N-oxide)-5,5',6,6'-4H,4'H-5,5'-bisimidazo oxadiazole (4), and the open-cage derivative of CL-20 (5)

Molecule	Pressure (GPa)	Shock Velocity (km/s)	Temperature (K)	Total Energy of Detonation (TNT eqv) (per cc)	(per gram)
1	27.514	8.104	3195.8	1.260	1.227
2	37.228	9.175	3671.5	1.644	1.442
3	38.487	9.281	3490.9	1.645	1.418
4	56.124	10.089	5344.1	2.307	1.884
5	38.878	9.362	3809.1	1.732	1.493

Based on these predictions, we began pursuing the synthesis of compounds **1**, **2**, **4**, and **5**. Due to the predicted sensitivity of compound **3**, we decided against synthesizing this EM. While compound **1** (Fig. 7) is known in the Russian literature,[9] the physical properties of this molecule have never been reported. Due to the presence of the cyclic ether, it is believed that this material could have interesting melt-cast capabilities. While the current synthesis of dinitramine **1** requires the use of energetic compounds throughout the entire synthesis, our synthetic approach, if ultimately successful, would represent a safer alternative, since the energetic transformations would occur only at the end of the synthesis.

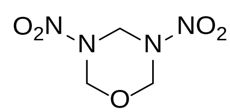
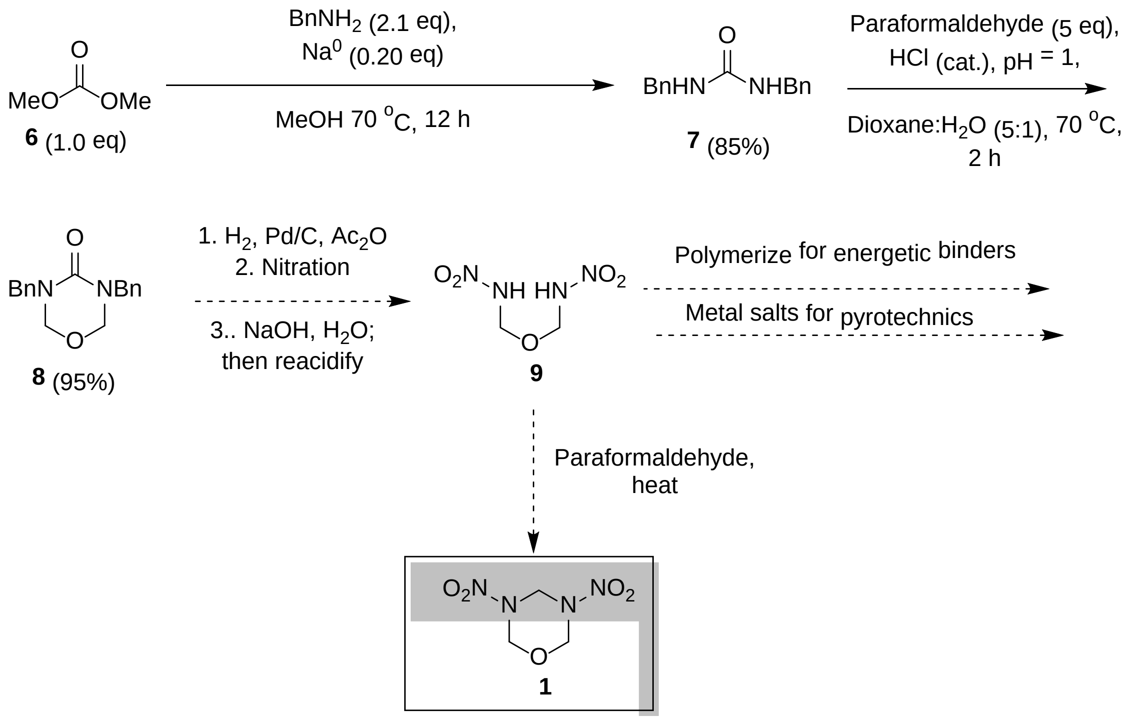


Fig. 7 3,5-dinitro-1,3,5-oxadiazinane (1)

The synthetic approach toward synthesizing dinitramine **1** is summarized in Scheme 1. Dibenzylurea (**7**) was synthesized in high yield by an environmentally friendly method without the use of phosgene reagents by reacting dimethyl carbonate and benzylamine with a catalytic amount of sodium methoxide. Treatment of urea **7** with an excess of paraformaldehyde under acidic conditions afforded cyclic ether **8**. The next step of the synthesis will be to subject cyclic ether **8** to hydrogenolysis, followed by nitration. Ring opening of the dinitrourea cyclic ether with NaOH, followed by reacidification of the disodium dinitramine salt would furnish dinitramine **9** as the open-chain. This material has potential to be a high performing EM. Dinitramine **9** can be subjected to polymerization to yield new energetic polymers. Alternatively, dinitramine **9** can be converted into alkali and alkaline earth dinitramine salts, which has pyrotechnic applications in civilian fireworks and military pyrotechnic illumination. Finally, treatment of dinitramine **9** with paraformaldehyde in the presence of heat would result in the desired cyclic ether dinitramine **1**.

Scheme 1. Synthesis of cyclic ether dinitramine **1**.



Turning to compound **2**, *bis*-adjacent RDX (Fig. 8), a compound that has never been reported in the literature and has appreciably higher predicted performance than RDX. RDX has a crystalline density of 1.80 cm^3, a detonation pressure of 34.7 GPa, and a detonation velocity of 8754 m/s.[10] The comparable performance of this molecule to HMX, and its predicted moderate sensitivity make it an interesting target for synthesis (NB: HMX has a crystalline density of 1.90 cm^3, a detonation velocity of 9150 m/s, and a detonation pressure of 39.3 GPa).[10]

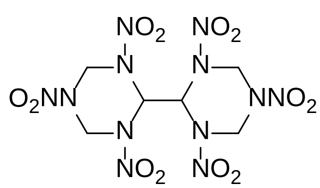
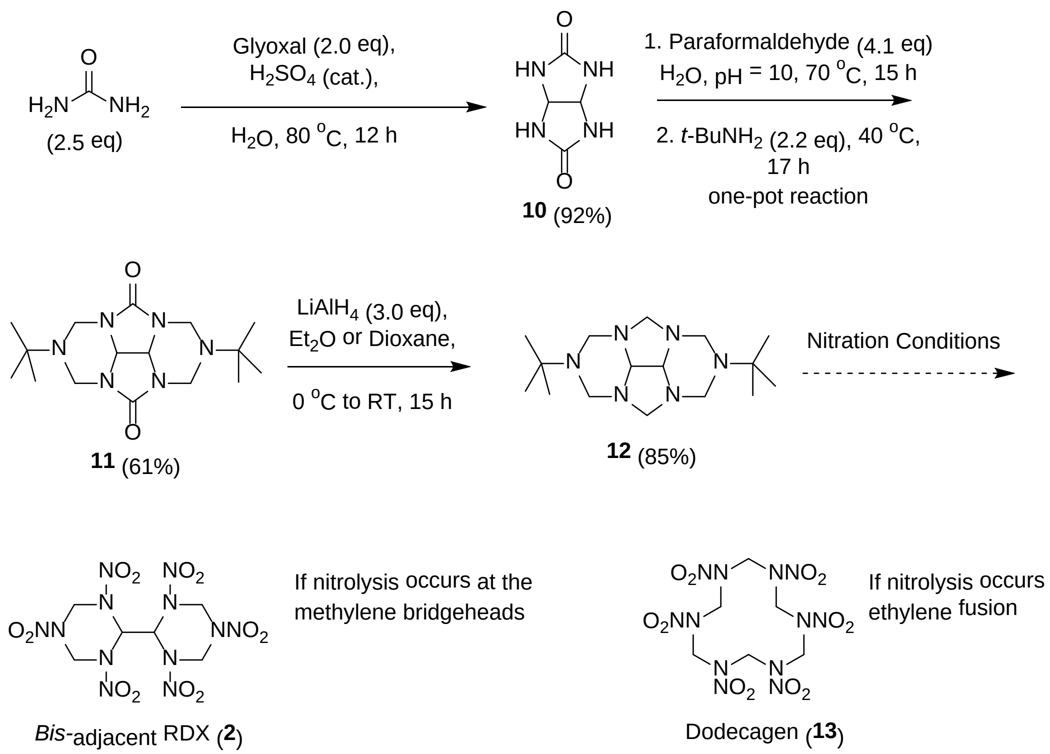


Fig. 8 ***Bis*-adjacent RDX (2)**

It was believed that glycoluril was a logical starting point toward the synthesis of *bis*-adjacent RDX. Glycoluril (**10**) was synthesized in high yield using the known acid-catalyzed condensation procedure between urea and glyoxal. With glycoluril in hand, a 1-pot method was developed to form tetracycle **11**. Paraformaldehyde was employed in a slight excess in slightly alkaline conditions to first afford the resulting glycoluril tetramethylol. This product was not isolated, but was instead treated with *t*-butylamine with moderate heating. This resulted in the formation of a white precipitate, which was filtered, and identified as tetracycle **11**. Conversion the diurea portion of tetracycle **11** to diaminal **12** was achieved in high yield using lithium aluminum hydride, see Scheme 2.

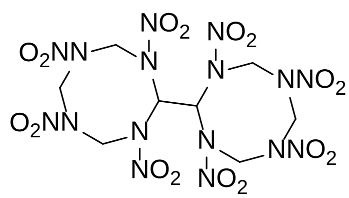
Scheme 2. Synthesis of *bis*-adjacent RDX.



With tetracycle **12** in hand, the stage is now set for nitration of this compound via the nitrolysis of methylene carbons. This logic is analogous to the Bachmann process, in which nitrolysis of methylenes occurs selectively on hexamine to afford RDX and HMX. In synthesizing bicyclo-HMX, it has been well established that a central hurdle in completing this synthesis was the ability for the fused 5-membered ring system to undergo ring-opening during nitrolysis depending on the nitration conditions used.[11] This phenomenon likely occurs as a way to relieve the ring strain of the fused 5-membered ring system. 6-membered rings, however, are the most thermodynamically stable, and it is not expected that nitrolysis will occur within the 6-membered rings with the 5-membered ring system present.

What is not known at this time is which direction nitrolysis will occur. If nitrolysis occurs at the methylene carbons of the bridgehead, then the product that forms would be *bis*-adjacent RDX (**2**). On the other hand, if nitrolysis occurs preferentially at the ethylene position of the ring fusion, then the product would be the 12-membered macrocycle dodecagen (**13**). This latter molecule has been described theoretically by McQuaid as having higher performance than HMX, with a crystalline density of 1.93 cm^3, a detonation velocity of 9230 m/s, and a detonation pressure of 37.0 GPa.[12] Undoubtedly, this latter molecule would be interesting, particularly if it could be synthesized in a handful of steps, as detailed in Scheme 2.

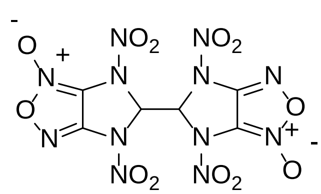
While compound **3**, *bis*-adjacent HMX (Fig. 9) has also never been reported in the literature and has a calculated performance similar to *bis*-adjacent RDX, as stated previously the predicted sensitivity of the former compound appears to be appreciably higher. It can therefore be debated as to whether synthesizing *bis*-adjacent HMX is a worthwhile target while other, similar performing yet less sensitive notional materials are possible. In light of the calculations performed within this report, it was decided that our synthetic efforts would be best focused elsewhere.



3

Fig. 9 *Bis*-Adjacent HMX (3)

Another compound that is currently in the process of being synthesized is *bis-N*-oxide (**4**), depicted in Fig. 10. This compound that has exceptionally high theoretical performance, yet calculates to have only a moderate sensitivity. Given the potential performance of this compound, it is imperative that *bis-N*-oxide (**4**) be synthesized successfully.

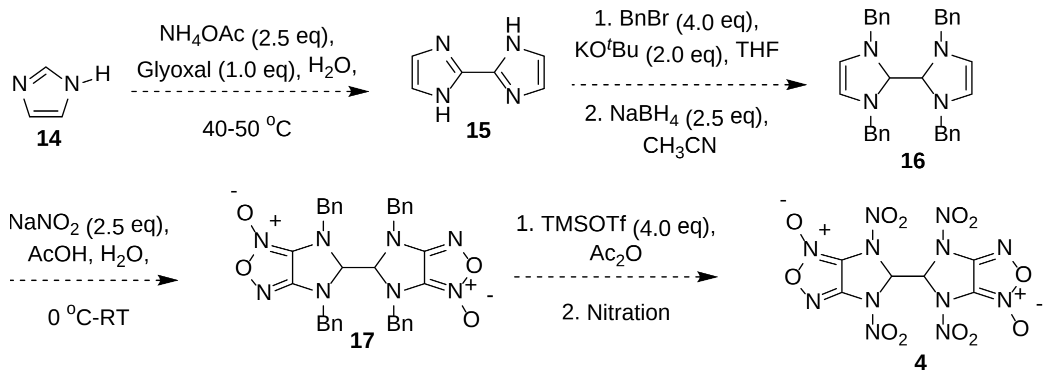


4

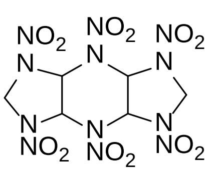
Fig. 10 4,4',6,6'-tetranitro-1,1'-bis(*N*-oxide)-5,5',6,6'-4H,4'H-5,5'-bisimidazo oxadiazole (4)

A proposed synthesis for *bis-N*-oxide (**4**) is summarized in Scheme 3. Imidazole (**14**) can be converted to bisimidazole **15** through a known procedure.[14] Subjection of this latter compound to benzyl bromide, followed by reduction of the resultant diimine with sodium borohydride[15] would yield tetrabenzylamine **16**. Exposure of the alkene moieties of tetrabenzylamine **16** with *in situ* generated N_2O_3 would afford *bis*-furoxan **17**. Conversion of the benzyl groups to the acetates, followed by nitrolysis would afford the sought after *bis*-*N*-oxide **4**.

Scheme 3. Synthesis of *bis*-*N*-oxide **4**.



Finally, the most elusive target thusfar has been a plausible synthesis for the open-chain version of CL-20 (Fig. 11). This molecule has better calculated performance than *bis*-adjacent HMX, and *bis*-adjacent RDX. Although it is calculated to be quite sensitive, as CL-20 is able to be synthesized and handled, it is believed that the open-chain version of the molecule, which is less strained, will also be able to be handled safely, assuming it can be synthesized.

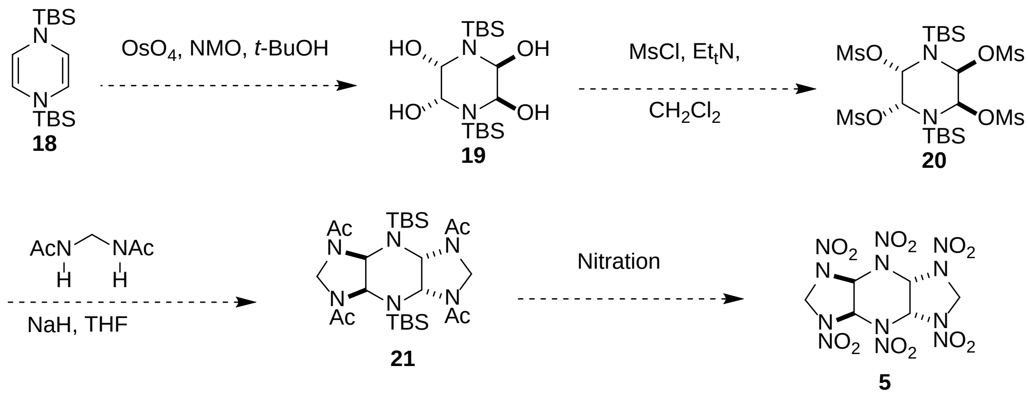


5

Fig. 11 Open-chain CL-20 (5)

A proposed synthetic pathway toward the synthesis of open-chain CL-20 is summarized in Scheme 4. Disilyl-1,4-dihydropyrazine (**18**) can be prepared from the known dissolving metal reduction route from commercially available pyrazine.[13] Osmium-catalyzed dihydroxylation of the diene via the Upjohn procedure would furnish tetraol **19** in the required *syn*-configuration, which could be converted to tetra-mesylate **20**. Reaction of this mesylate with methylene *bis*-acetamide, followed by global nitration would yield **5**; the open-chain version of CL-20.

Scheme 4. Synthesis of open-chain CL-20.



3. Conclusions

The ARL-developed software tools were used to predict the heats of formation and crystalline densities of notional compounds **1–5**. Using this predicted data, we then ran Cheetah calculations to predict the performance of these novel materials. Additionally, we predicted the qualitative impact sensitivity of these compounds using electrostatic potential maps. Based on the theoretical models, synthetic efforts were initiated for compounds **1** and **2**, and synthetic pathways to make compounds **4** and **5** were provided. Due to the high predicted sensitivity, coupled with inadequate performance compared to *bis*-adjacent RDX, *bis*-adjacent HMX (**3**) was not considered further for synthesizing. *Bis-N*-oxide **4** was determined to be a very powerful potential explosive, with a density of 2.025 cm^3, a detonation pressure of 56.124 GPa, and a detonation velocity of 10.089 km/s. Efforts to synthesize this molecule, as well as molecules **1**, **2**, and **5** continue.

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List of Symbols, Abbreviations, and Acronyms

Ac	Acetyl
APG	Aberdeen Proving Ground
ARL	US Army Research Laboratory
Bn	Benzyl
CH_2Cl_2	Methylene Chloride
DFT	Density functional theory
CJ	Chapman-Jouguet
DSRC	Department of Defense (DOD) Supercomputing Resource Center
EM	Energetic Material
ESP	electrostatic surface potential
Et	Ethyl
cm^3	grams per cubic centimeter
HCl	hydrochloric acid
HEDM	High Energy Dense Material
kcal/mol	kilocalories per mole (unit of energy)
KS-DFT	Kohn-Sham density functional theory
NaOH	sodium hydroxide
NMO	*N*-morpholine-*N*-oxide
Ms	Methanesulfonyl
t-Bu	*tert*-butyl
THF	Tetrahydrofuran
TBS	*tert*-butyldimethyl silyl
Tf	Triflate
TMS	Trimethylsilyl

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J MORRIS
B RICE
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J SABATINI
W SHERRILL
J BANNING
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